SESQUITERPENE LACTONES OF TWO SPECIES OF ARTEMISIA

A. Ovezdurdyev, S. Kh. Zakirov, M. I. Yusupov,
Sh. Z. Kasymov*, A. Abdusamatov, and V. M. Malikov

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In the present paper we give the results of an investigation of the sesquiterpene lactones of Artemisia absinthium L. (common wormwood) and A. argyi L.

The epigeal part of A. absinthium gathered in Tashkent province was extracted with ethanol. The concentrated extract was purified with 35% aqueous ethanol. The precipitate that deposited was separated off and the compounds to be investigated were extracted from the filtrate with ethyl acetate. When the ethyl acetate extract was chromatographed on a column of KSK silica gel, two crystalline substances were isolated. Substance (I), isolated from benzene fractions, had the composition $C_{15}H_{18}O_4$, mp 230-232°C (benzene—ether), M^+ 262. The IR spectrum of (I) had absorption bands at (cm^{-1}) 1770 (γ-lactone carbonyl), 1675 (α,β-unsaturated ketone), 1630 and 1620 (double bonds), and 3360 (hydroxy group).

Elution of the column with chloroform—acetone (9:1) yielded substance (II) with the composition $C_{15}H_{18}O_3$, mp 218-220°C (ethanol), M^+ 246. The IR spectrum of (II) showed absorption bands at (cm^{-1}) 1590, 1610, 1665, 1720, and 3100-2500 cm^{-1}. The NMR spectrum of (II) (Py-d_5) showed the signals of a secondary methyl group, of two tertiary methyl groups, and of olefinic protons.

From its physicochemical properties and spectral characteristics, substance (I) was identified as the sesquiterpene lactone parishin C [1, 2], and (II) as the sesquiterpene lactone parishin B [2, 3].

A report has been given previously of the isolation from chloroform extracts of the epigeal part of A. argyi L. of three sesquiterpene lactones: chrysartemin B, canin, and isoridentin [4]. The benzene fractions after the isolation of the above-mentioned lactones were combined, and by rechromatography on a column of alumina two crystalline compounds, (III) and (IV) were isolated.

Compound (III), isolated from fractions eluted with benzene—hexane, had the composition $C_{17}H_{20}O_5$. M^+ 304, mp 190-192°C (hexane—acetone). The IR spectrum of (III) contained the absorption bands characteristic for a γ-lactone carbonyl (1785 cm^{-1}), and ester group (1743 and 1240 cm^{-1}), an α,β-unsaturated ketonic carbonyl (1685 cm^{-1}), and double bonds (1640 and 1622 cm^{-1}). The UV spectrum showed a maximum at 248 nm (log ε 4.15), which is characteristic for a dienone group.

In its composition, properties, and spectral characteristics, compound (III) was similar to the isomeric sesquiterpene lactones matricarin and artilesin [5, 6]. For complete identification, matricarin was obtained by the acetylation of austricin. Compound (III) was identical with matricarin according to its IR spectrum and the absence of a depression of a melting point of a mixture. When the column was eluted with benzene, a colorless crystalline compound (IV) with the composition $C_{15}H_{20}O_3$, mp 190-191°C (ethyl acetate—hexane), M^+ 248, was isolated. The IR spectrum of (IV) showed the absorption bands of a carbonyl group in a γ-lactone ring (1745 cm^{-1}), of a hydroxy group (3470 cm^{-1}), and of double bonds (1660 cm^{-1}). From its physicochemical constants and a direct comparison of IR spectra, substance (IV) was identified as the sesquiterpene lactone khanphyllin [7].

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ISOPRENOIDS OF THE OUTER BARK OF THE FAR EASTERN BIRCHES Betula costata AND Betula ermanii

T. Yu. Kochergina, G. V. Malinovskaya,
N. D. Pokhilo, and N. I. Uvarova

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Continuing an investigation of the chemical composition of Far Eastern birches [1, 2], we have studied extracts of the outer bark of *Betula castata* Trautv., which is widespread in the southern part of the Far East (samples 1-4) and *B. ermanii* Cham. (Erman's birch) growing on Kamchatka, Sakhalin, and the Kurile islands (sample 5). Both species of birch belong to the subgenus Neurobetula V. Vassil. [3].

The air-dried bark was extracted with chloroform in a Soxhlet apparatus for 14 h. The dry residue obtained by evaporation in vacuum was separated on a chromatographic column of KSK silica gel using the solvent system petroleum ether—acetone. This led to the isolation of β-sitosterol (I) and eight triterpenoids: 3β-acetyl-11α,12α-epoxyolean-28,13-olide (II) [4], the acetate of oleanolic acid (III), lupeol (IV), methyl oleanolate (V), betulin (VI), betulinic acid (VII), oleanolic (VIII), and betulin caffeate (IX). Compounds (VI-IX) were isolated after the acetylation of the fraction containing a difficultly separable mixture of these components.

Extracts of the bark of *B. costata* and *B. ermanii* (samples 2 and 5) showed antioxidant activity according to the method of Maximov et al. [5]. The activity of these samples is obviously connected with the presence of betulin caffeate [6], since this component was present only in summer samples of the bark. The results of the investigation are given in Table 1. The structures of the compounds isolated were confirmed by mixed melting points with authentic samples (no depression of the melting points was observed) and by comparison of their IR spectra.

TABLE 1.

Sample and time of collection	Yield of extract	Yield of the composition, % of the total air-dried bark								
		I	II	III	IV	V	VI	VII	VIII	IX
B. costata										
9. V 1986	15,15	—	0,019	0,3	0,19	—	3,00	—	1,5	—
18. VI 1984	15,6	0,027	—	0,7	0,13	0,015	2,44	0,08	1,4	0,04
14. IX 1984	23,4	—	—	0,55	0,11	0,016	5,27	—	1,23	—
20. XII 1984	17,7	—	—	0,3	0,16	—	2,94	—	1,41	—
B. ermanii										
26. VIII 1984	21,0	—	—	0,42	0,23	—	2,37	—	1,12	0,26

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